Colloidal Processing and Freeze Casting for Net-Shaping

Kathy Lu
Chris Kessler
Xiaojing Zhu

CNMS User Facility Collaborator: Rich Kasica

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Nanomaterial Fabrication Approaches

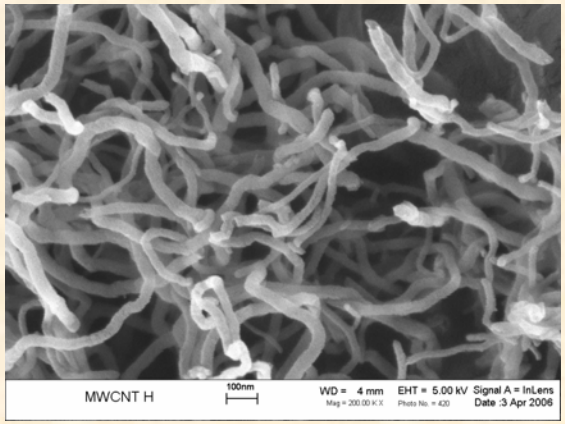
- Top-down Approach
  - Lithography (focused ion beam lithography, electron beam lithography)
  - Imprint lithography
  - Electrochemical approach
- Bottom-up approach
  - 0D: nanoparticles
  - 1D: nanotubes, nanowires, nanorods
  - 2D: nanofilm, nanocoating
- **3D particulate nanomaterials bridge these aspects and have extremely promising application potentials**

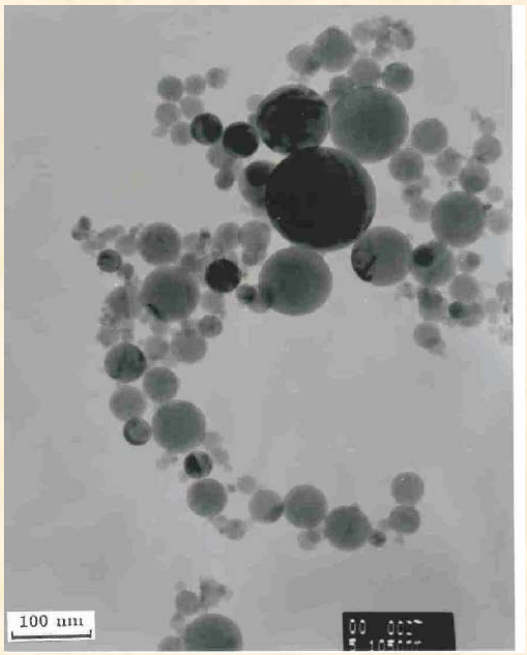
Motivation

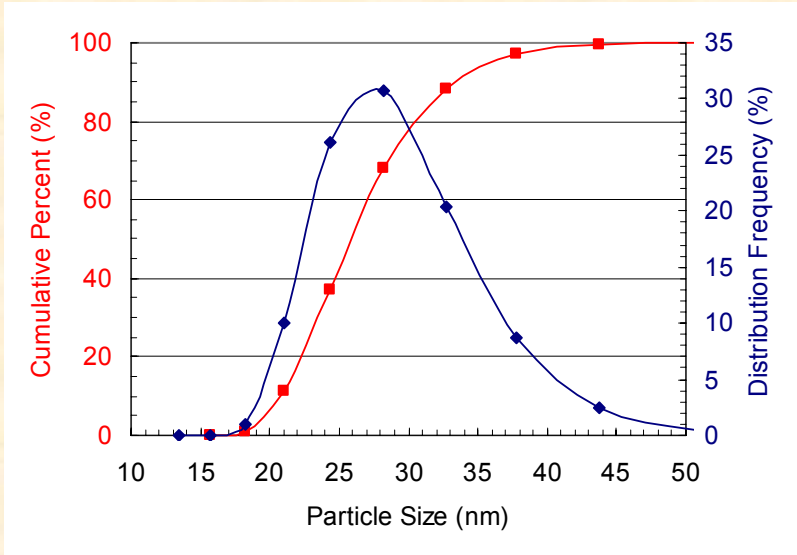
- Use mostly water to create stable nanoparticle suspensions of high solids loading while avoiding complicated organic removal/drying processes
- Develop an inexpensive, easy-to-use forming process for nanostructured ceramics—freeze casting
- Make complex near-net shapes

Suspension System

- Al_2O_3 Nanoparticles, (Nanophase Technologies, Romeoville, IL)
- TEM, Zetasizer NS, d_{50}=27.5 nm
- Carbon Nanotube, Helix Material Solution, Richardson, TX)

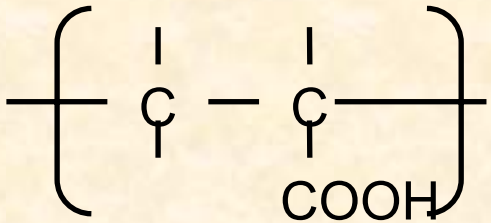




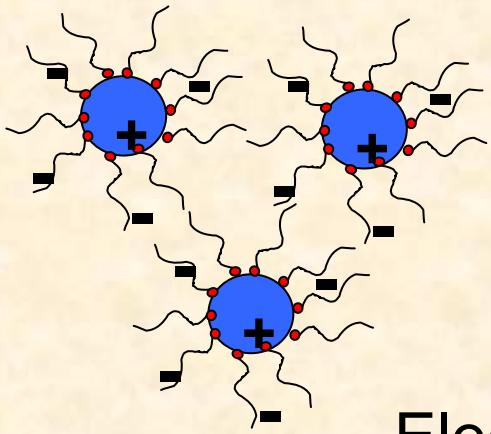


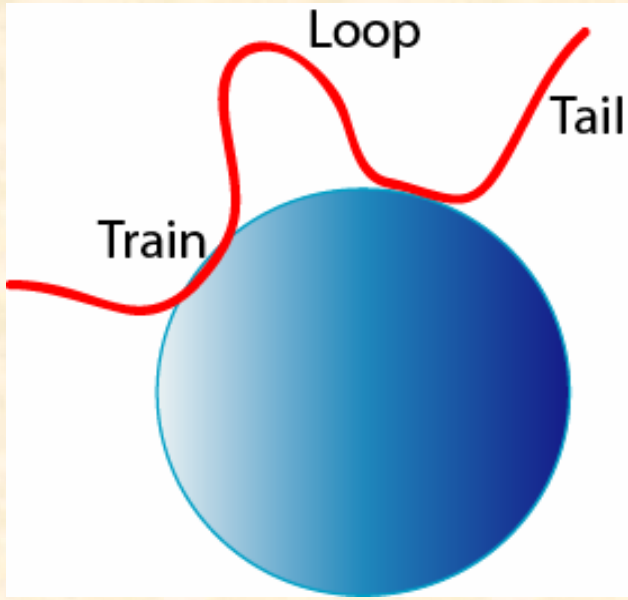
Suspension System, cont'd

- Poly(acrylic acid) [PAA], M_W 1,800 (Aldrich, St Louis, MO)



- NH_4OH & HCl used to adjust pH
- Glycerol (Fisher Chemicals, Fairlawn, NJ)

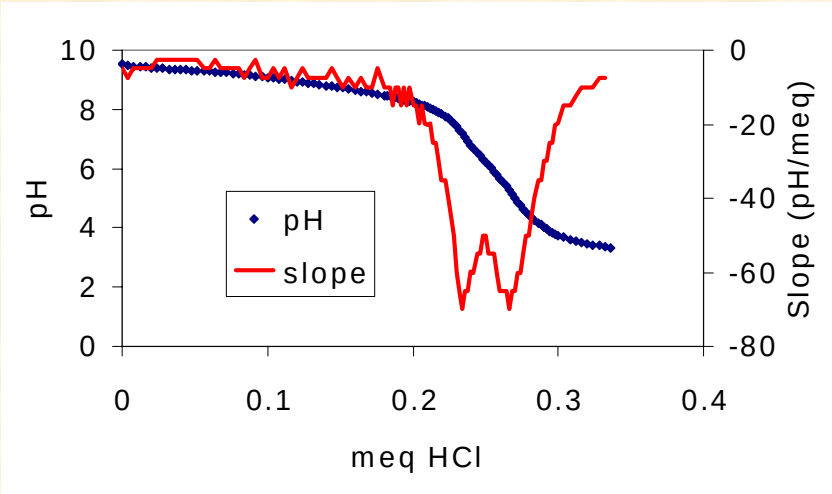


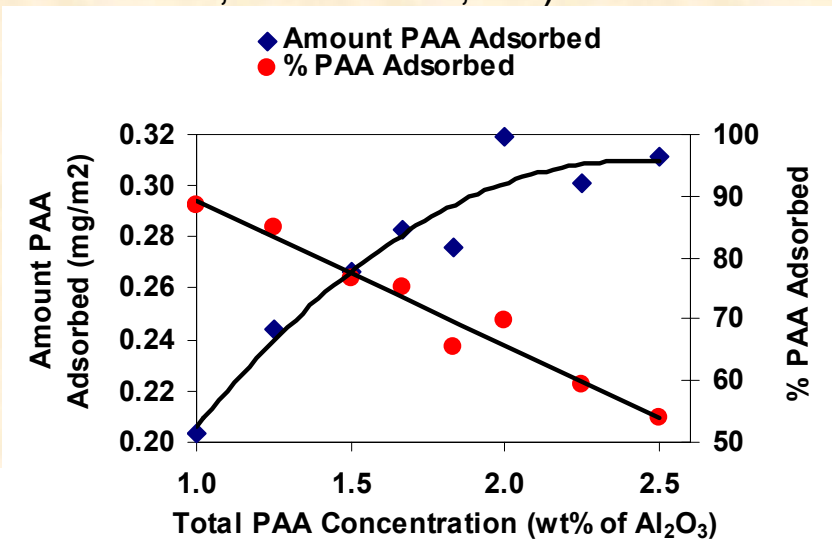


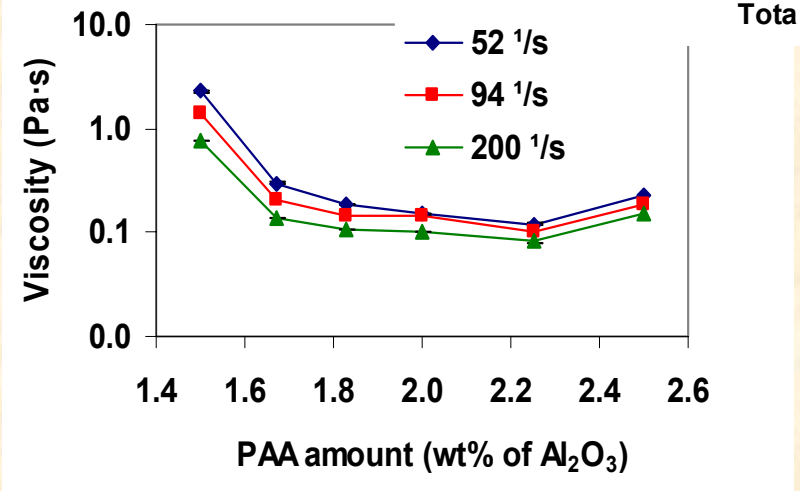
Electrosteric Stabilization

Optimization of Dispersant

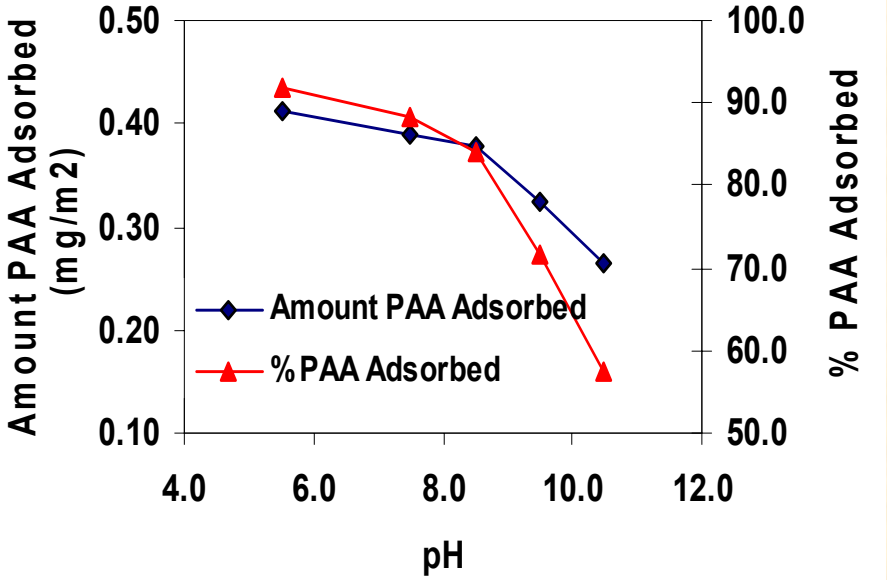
- Suspensions: pH = 9.5, 30 vol% Al_2O_3
- Evaluation criteria
  - PAA adsorption: Potentiometric titration
  - Viscosity, AR2000 Rheometer (TA Instruments, New Castle, DE)

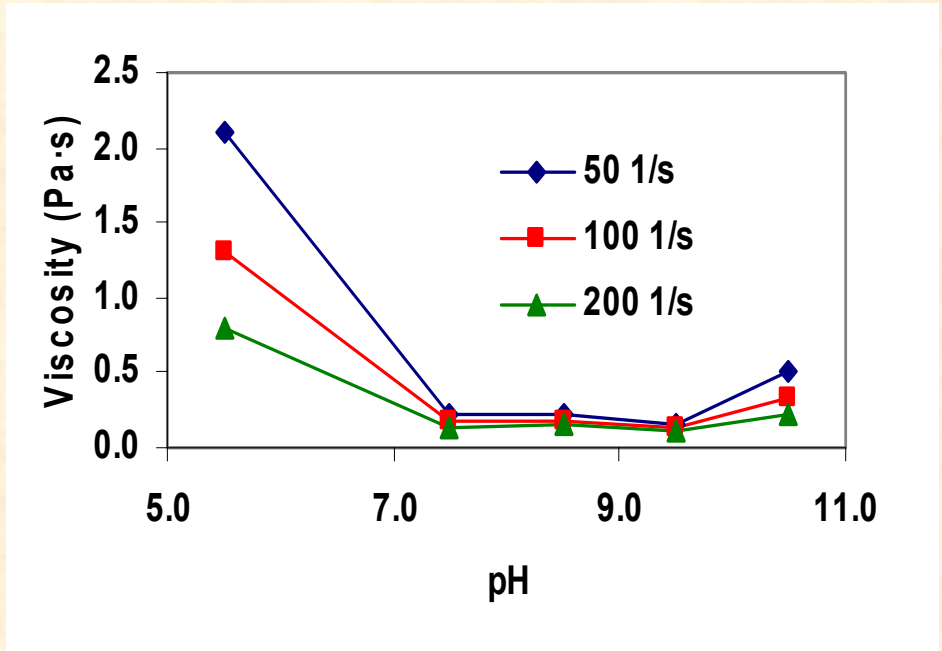






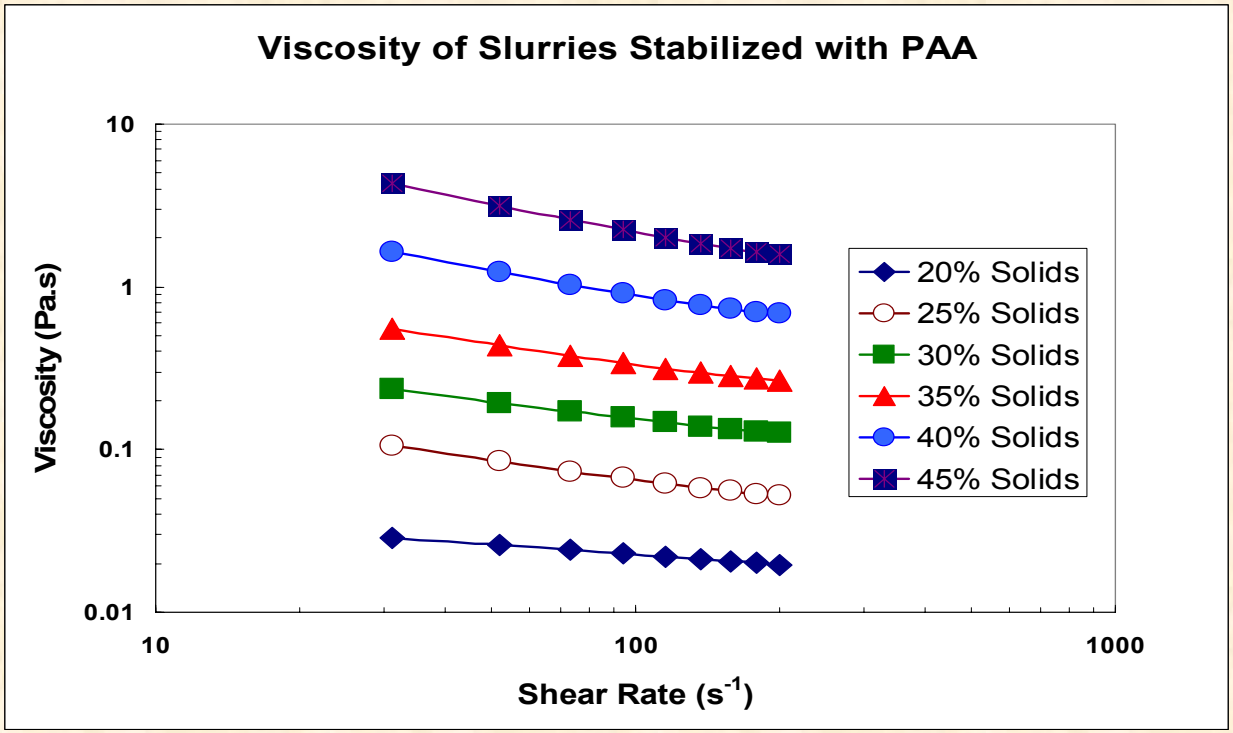
Optimization of pH





- Suspensions of 30 vol% Al_2O_3, 2.0 wt % PAA
- Valley of low viscosity between pH 7.5-9.5

Solids Loading and Viscosity



- Viscosity of Al_2O_3 suspensions at 20-45% solids loading
- Viscosity increases as solids loading increases but 45% solids loading is achieved

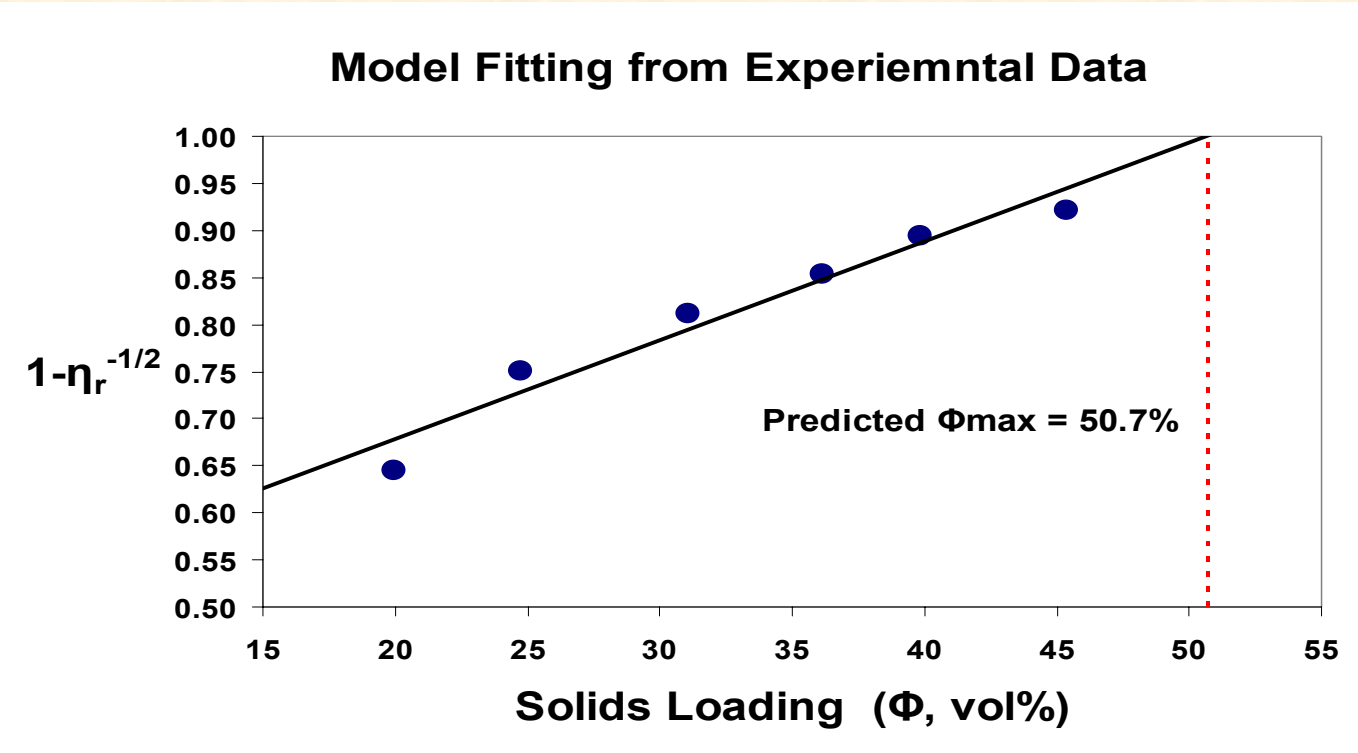
Theoretical Solids Loading Limit

- Suspension solids loading has direct effect on green density
- Viscosity →solids loading → green density
- $\eta_r = [1 - (\Phi/\Phi_m)]^{-[\eta]\Phi_m}$
  - » $\eta_r = \eta_s / \eta_0$: Relative viscosity
  - » $[\eta]$: Intrinsic viscosity
  - » Φ: Solids loading
  - » Φ_m: Maximum solids loading
- Assume that at Φ_m viscosity approaches infinity.
  - Model relative viscosity by $1 - \eta_r^{-1/n} = a\Phi + b$*
  - Use empirical data to extrapolate Φ_m where η_r is infinite

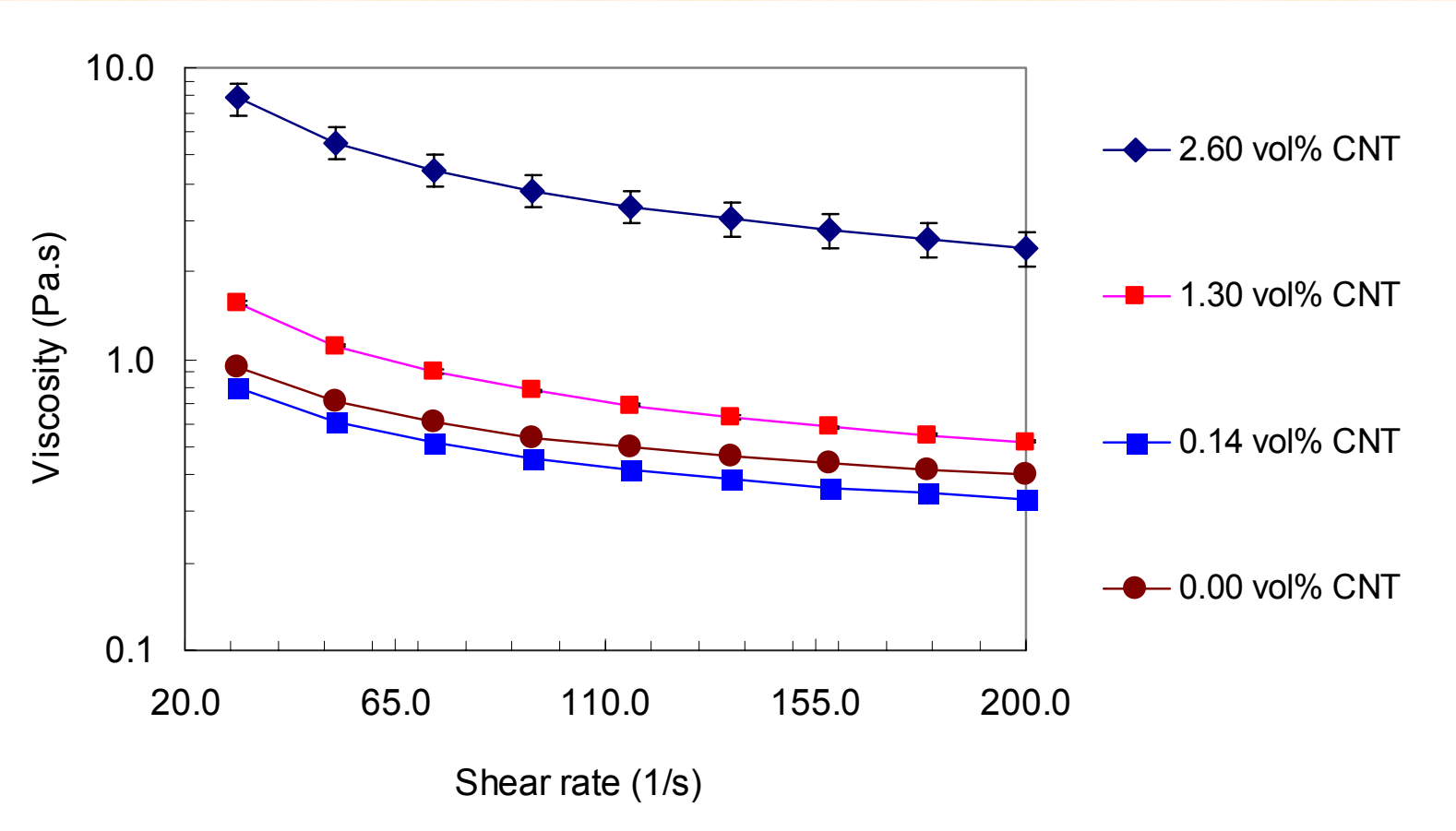
*D Liu, *J Mat Sci* 35 (2000) 5503-5507

Viscosity vs Solids Loading

- Assumptions:
  - At a shear rate ~100 s^{-1}, [η] = 2
  - Model applicable over a wide solids loading range 20-60 vol%
- Extrapolated Φ_m = 50.7 vol%



CNT Effect on Suspension Viscosity



- A threshold CNT value for substantial rheology change, 1.3 vol%

Freeze Casting

- Suspension of 40 vol% solids loading was poured into silicone mold
- Freeze-cast in Labconco Stoppering Tray Dryer (Labconco, Kansas City, MO)

- Frozen at -35°C for 2 hours
- Pressure decreased to $<10^4$ Pa for 36 hours

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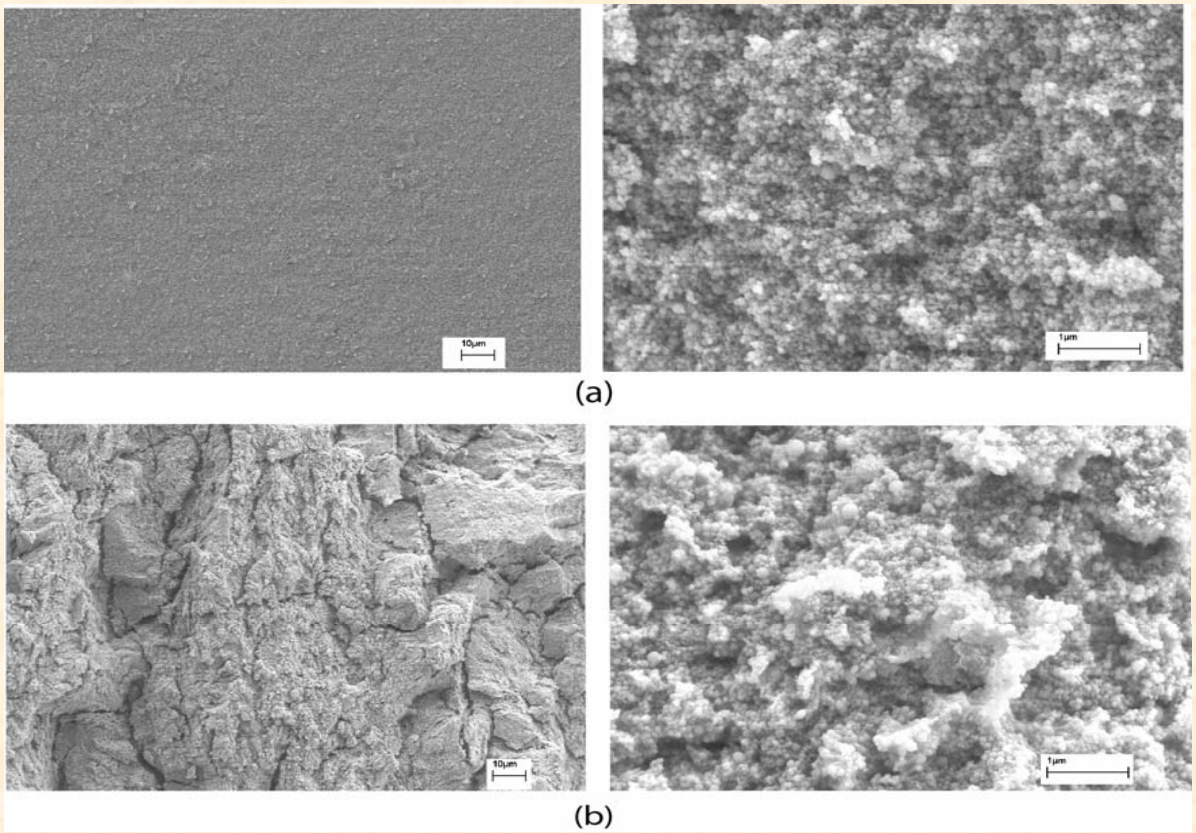
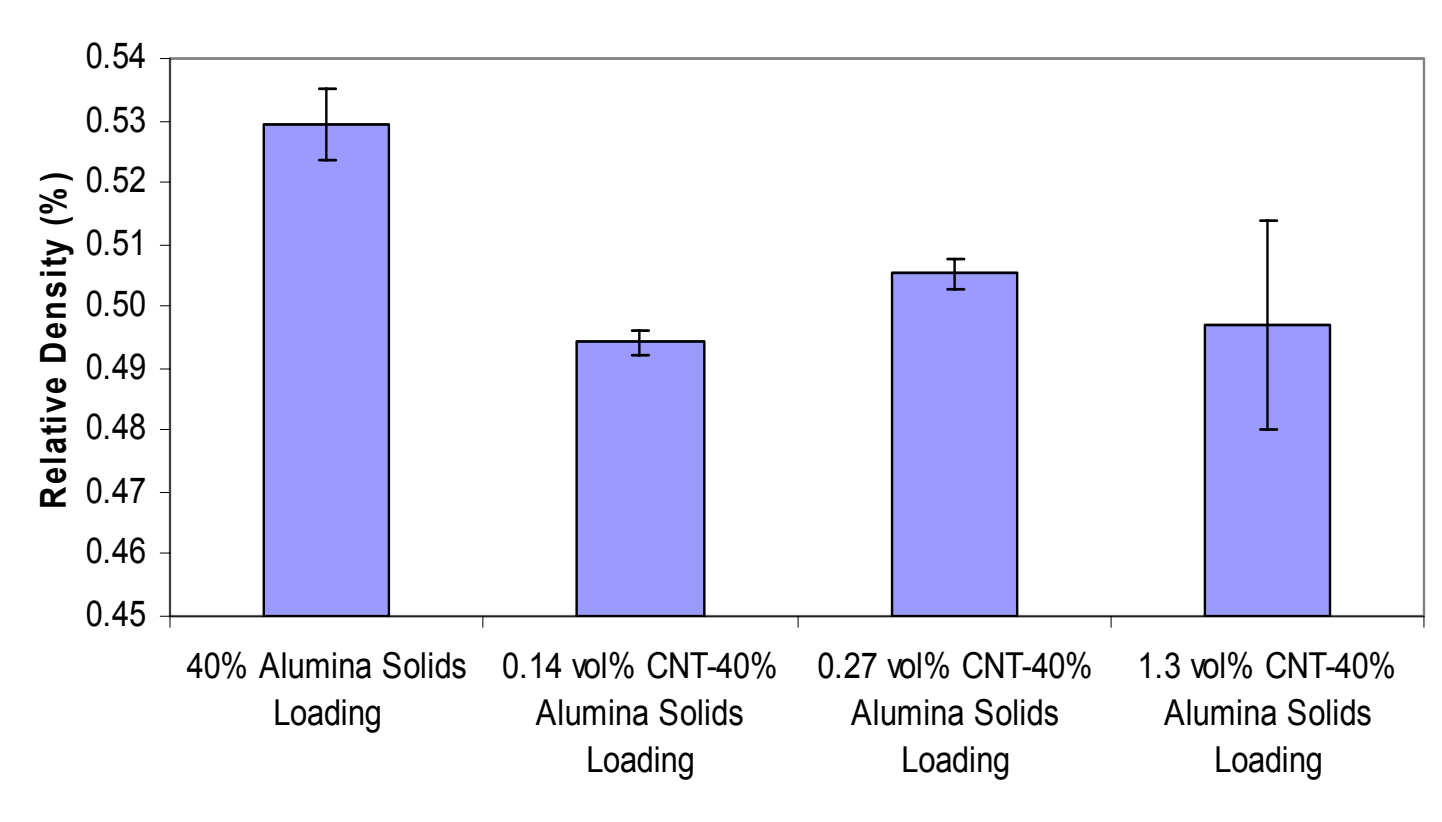
Green Microstructure



(a) with pre-rest stabilization, (b) with no pre-rest stabilization

53% green density is achieved after freeze drying

Relative Density



Conclusions

- Optimal suspension conditions are pH 9.5, 2.0 wt% PAA
- Theoretical maximum solids loading is estimated at 50.7 vol% Al_2O_3
- Experimentally was able to achieve 45 vol% solids loading
- Suspensions of 40 vol% Al_2O_3 w/ and w/o CNTs were freeze cast successfully
- Freeze dried sample had ~53% density for 40 vol% Al_2O_3 suspension, CNT- Al_2O_3 sample has ~50% solids loading.

Future Work

- Continue to improve suspension properties in order to increase solids loading and eventually green density
- Assemble multiple compositions into complex geometries
- Sintering densification & new properties such as suppressing grain growth and introducing conductivity
- Direct device fabrication